

Angle Resolved Soft X-ray Spectroscopy in Emission and Absorption

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X-ray Emission and Absorption

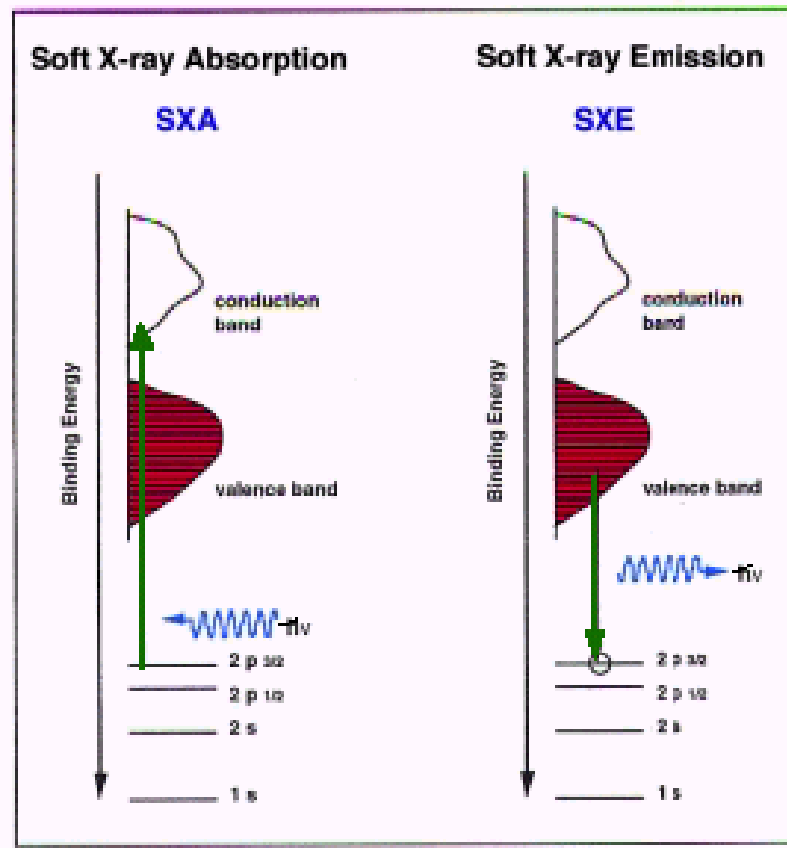


Fig. 11. Schematic representation of the core-electron absorption process (left) and the soft x-ray emission process (right). Both transitions are described by optical dipole matrix elements.



Why X-ray Fluorescence?

- Site specificity
- Probes bulk properties
- Study buried materials
- Photons are not affected by E-M fields
- Use polarization
- NEXAFS
- Raman Scattering Cross sections can be large in the soft x-ray range.



Why X-ray Fluorescence?

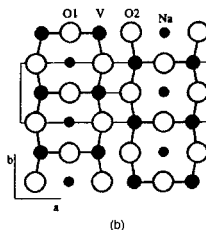
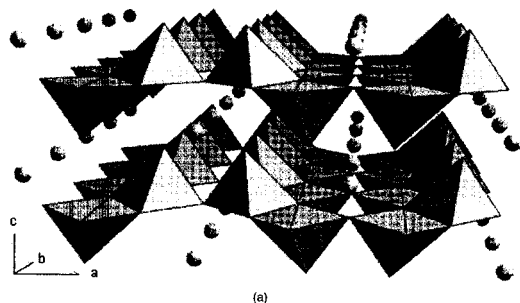
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- Raman Scattering Cross sections can be large in the soft x-ray range.



**Angular Resolved Spectroscopy of
 NaV_2O_5 & Sr_2RuO_4
or
Will Angular Resolved Data Add a New
Dimension?**



Angular Resolved Spectroscopy of NaV_2O_5

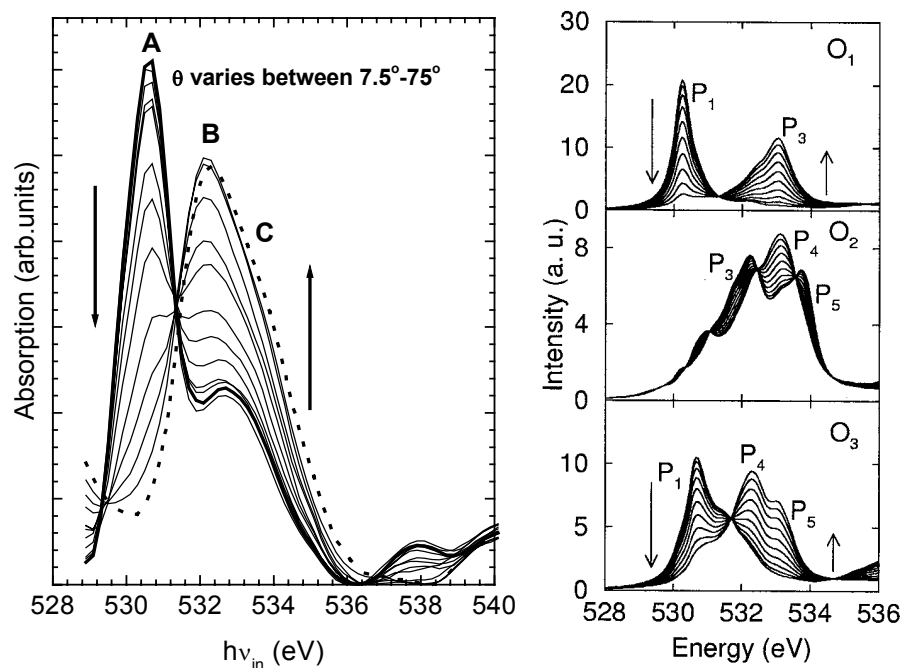


a) The structure of NaV_2O_5 . Oxygen atoms are located at the 5 corners and V at the center of each VO_5 pyramid. (b) O1 atoms bridge the V atoms forming the rung of each double chain. O2 atoms join ladders above and below the a-b plane. O3 atoms occupy the apical position in c direction for each pyramid.

- Angular variation of absorption spectra depends on orientation of polarization vector with electronic density in real space for each electronic bonding state.



Angular Resolved Spectroscopy of NaV_2O_5 : Absorption

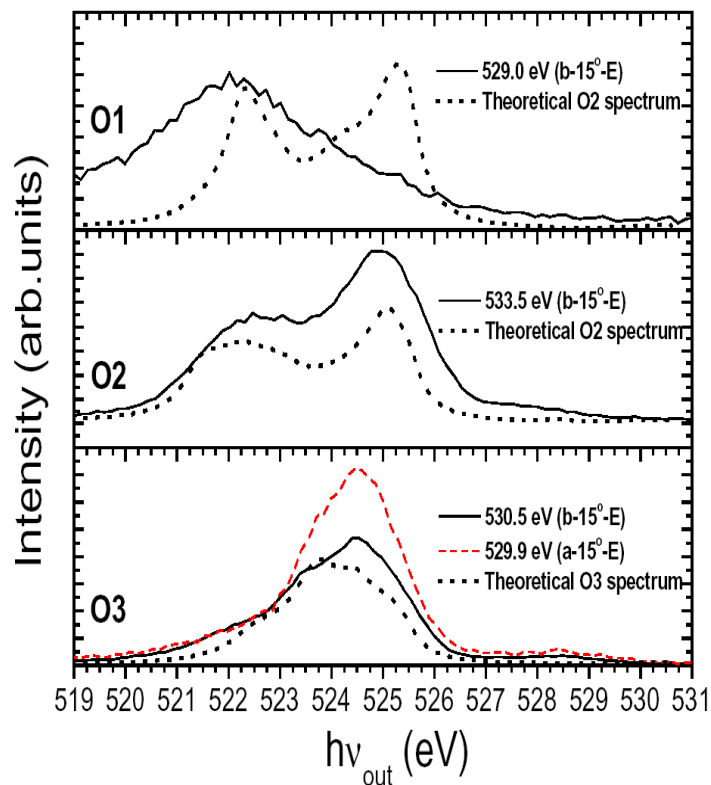


- Angular variation maps orbital orientation in real space.

- Figure (a) The O-K absorption spectra for NaV_2O_5 taken as a function of incident angle. The angles are measured from the b-axis in the bc plane. (b) Calculations of the absorption spectra for each oxygen site as a function of the angle from the b axis in the bc plane



Angular Resolved Spectroscopy of NaV_2O_5 : Emission



- The site selected O-K fluorescence spectra for NaV_2O_5 . Experimental spectra are compared with calculated site selected partial density of states.
- Very good agreement is obtained for the O2 (chain) and O3 (apical) sites. For the O1 (rung) site, the high energy structure in the theoretical spectrum is sharply suppressed. This spectrum is taken below threshold in the RIXS regime and thus is a RIXS rather than a normal fluorescence spectrum. We believe that the suppression of the higher energy portion of the spectrum is associated with the selection rule against excitation between spatially symmetric and anti-symmetric states that is known to effect RIXS spectra.



Angular Resolved SX Spectroscopy: Sr_2RuO_4

Structure of Sr_2RuO_4 and $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ two remarkable materials

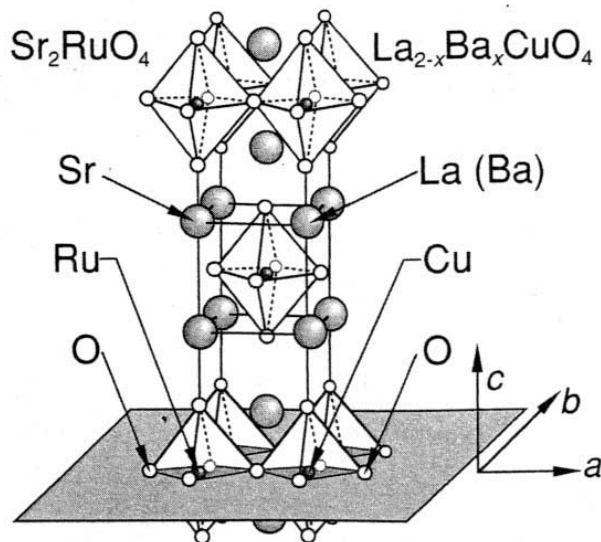
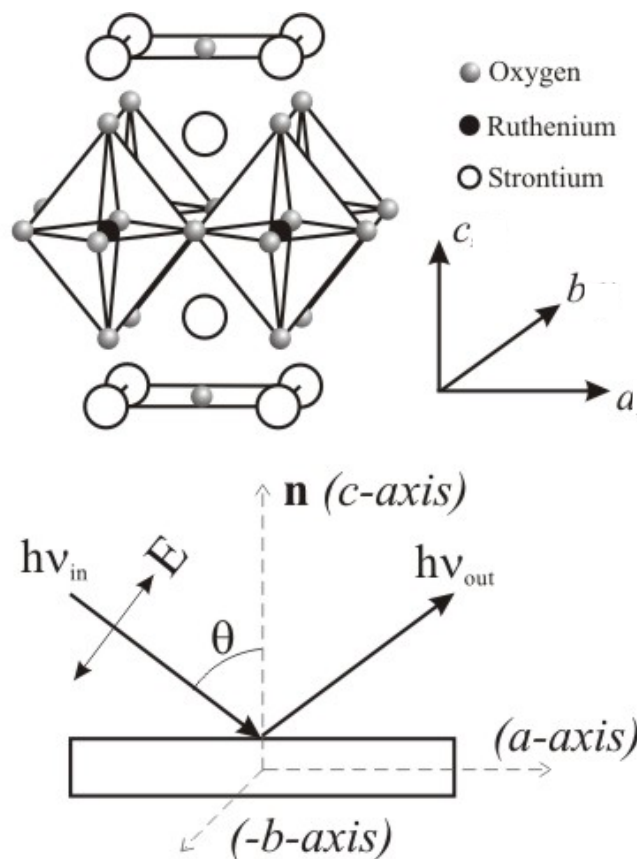


FIG. 1. The layered perovskite structure common to ruthenate and cuprate superconductors.

A.P. Mackenzie, and Y. Maeno,
Rev. Mod. Phys. 75, 657,(2003)



Experimental Configuration



XES and XAS of Sr_2RuO_4

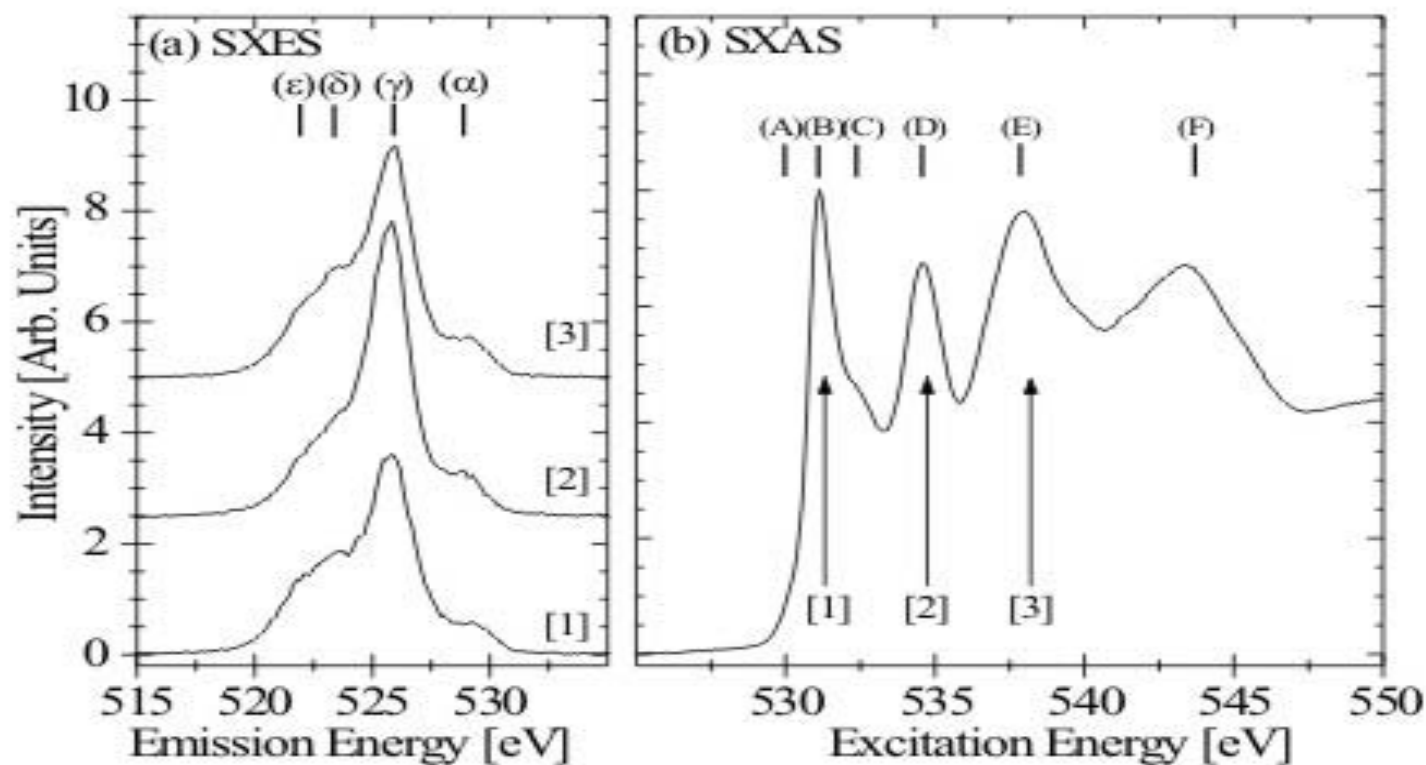


Figure 5.5. RXES (a) and SXAS (b) spectra of Sr_2RuO_4 measured at an incident angle of 45 degrees.



Angular Dependent XAS and XES of Sr_2RuO_4

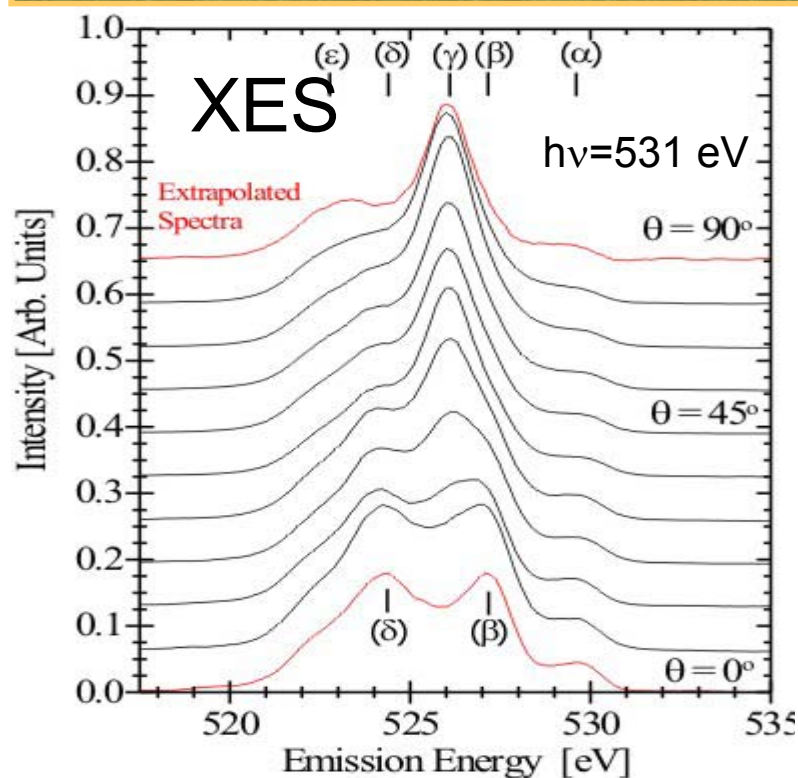


Figure 5.12. Angle-resolved soft x-ray emission spectroscopy measurements of Sr_2RuO_4 rotated about the b crystal axis.

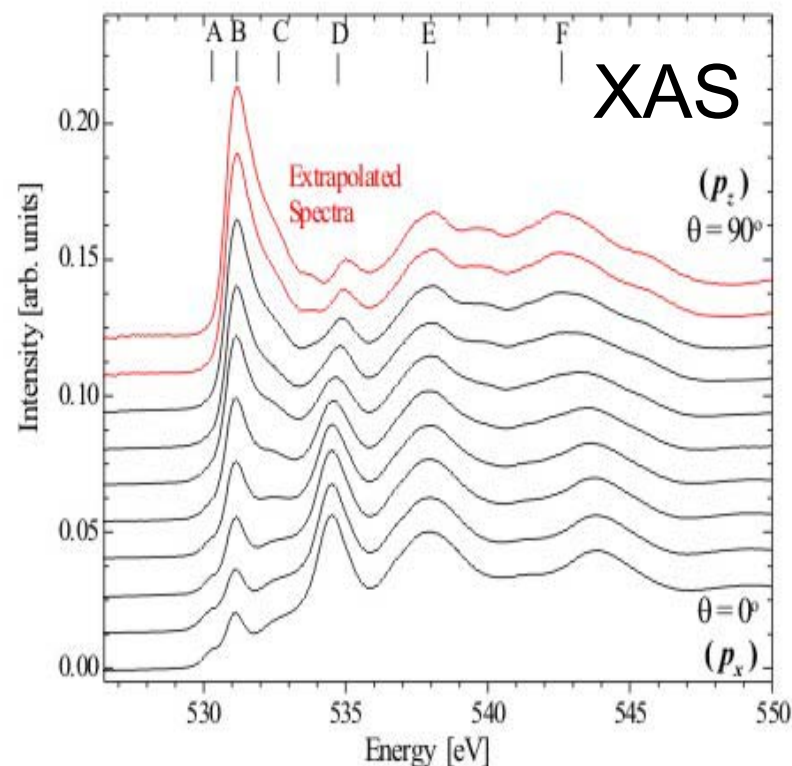


Figure 5.8. Angle-resolved soft x-ray absorption spectroscopy measurements of Sr_2RuO_4 rotated about the b crystal axis.



Calculated Partial Density of States for Sr_2RuO_4

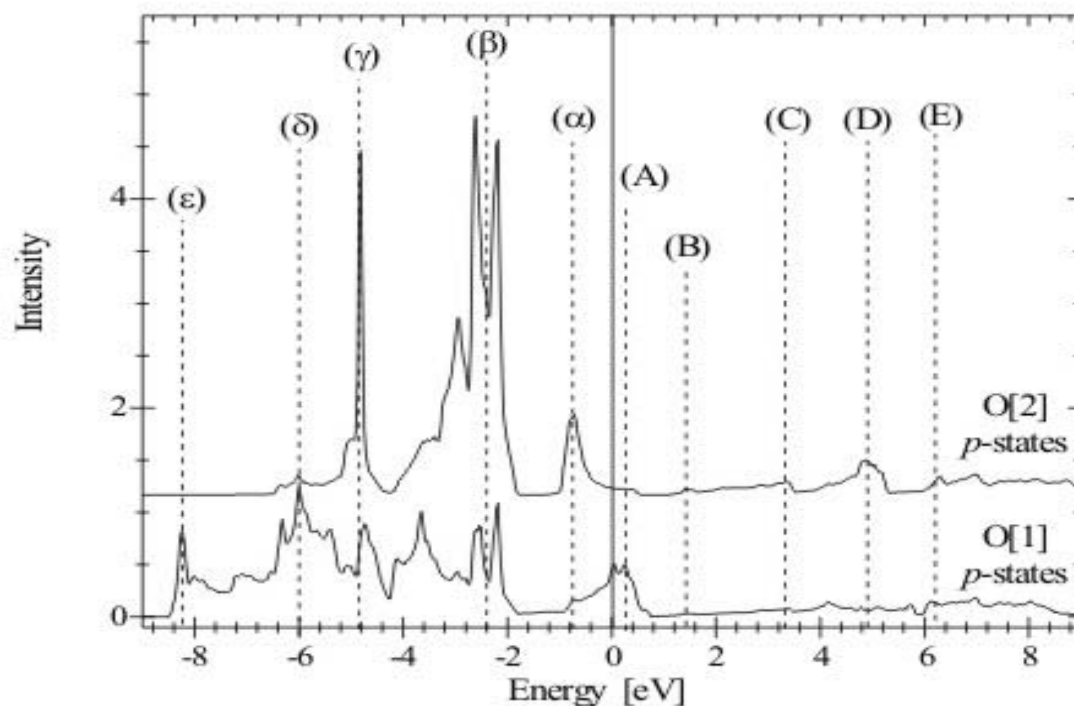


Figure 5.6. Partial density of O p -states for O[1] and O[2] atomic sites in Sr_2RuO_4 with dashed lines denoting the states responsible for the SXAS and SXES peaks from Figure 6.5.



Calculated PDOS of P_x , P_y , P_z at the O(1) and O(2) Sites

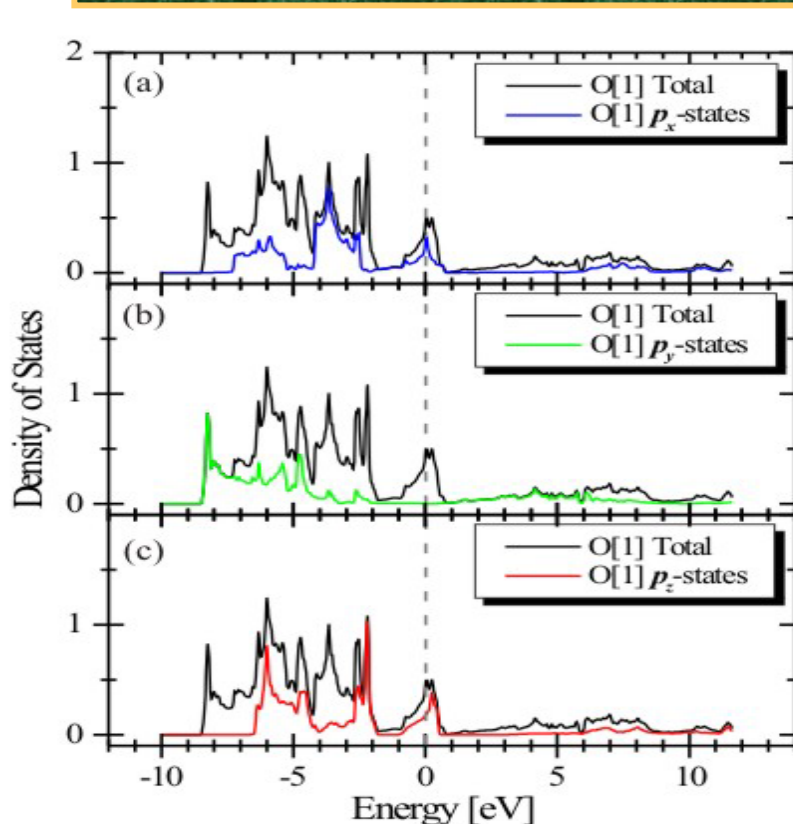


Figure 5.3. The density of p -states for the planar (O[1]) atoms in Sr_2RuO_4 , divided into the (a) x , (b) y , and (c) z orientations of the p -orbitals.

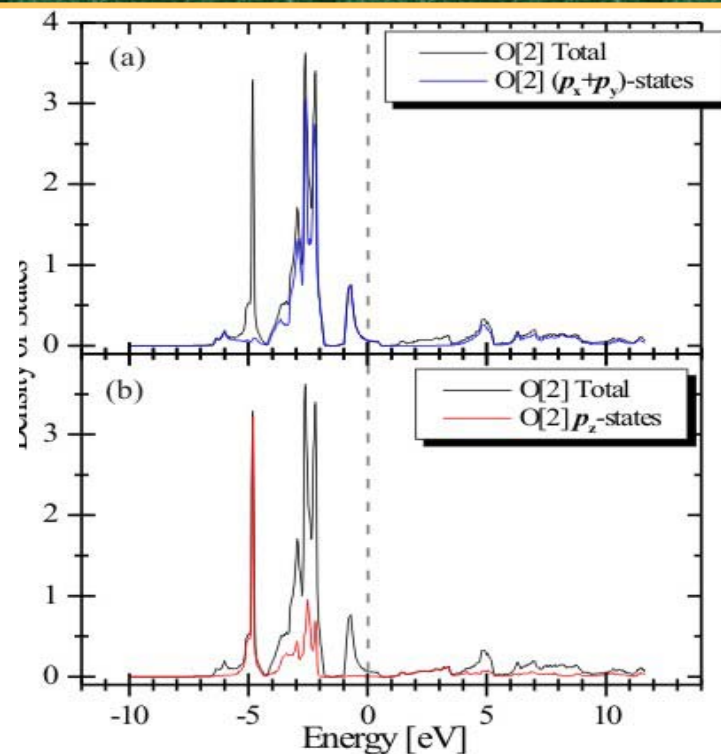


Figure 5.4. The partial density of O p -states for the apical oxygen (O[2]) atoms in Sr_2RuO_4 , divided into the (a) $x+y$, and (b) z orientations of the p -orbitals. Due to the higher (tetragonal) symmetry of the O[2] site, the x and y orientations can only be represented by their combined DOS and cannot be individually determined.



NEXAFS of Sr_2RuO_4 : Theory and Experiment

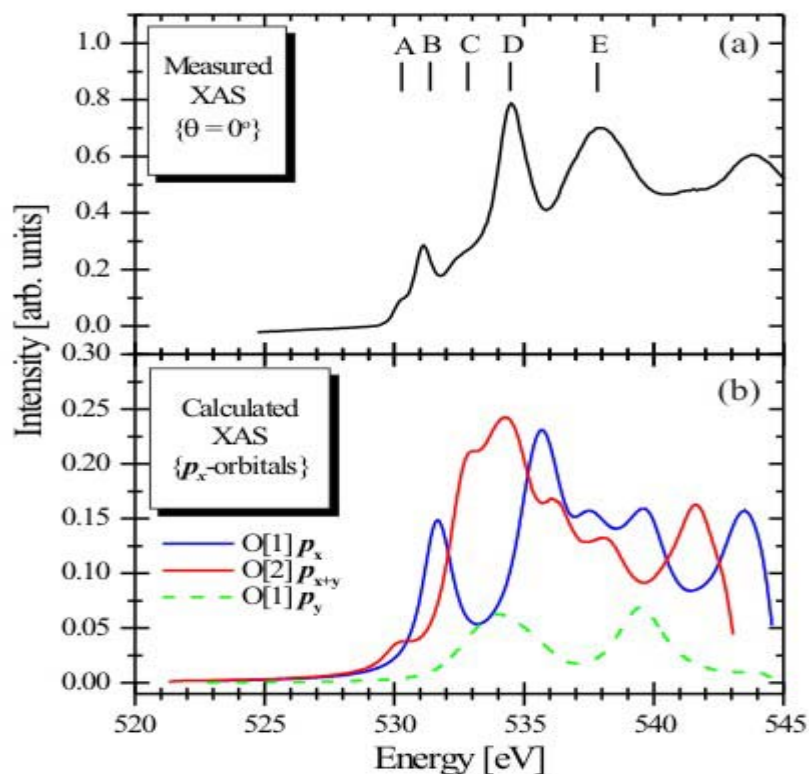


Figure 5.10. Comparison of (a) the experimental absorption spectra targeting the p_x orbitals ($\theta = 0$ degrees) with (b) the calculated absorption spectra of the p_x and p_y orbitals of the O[1] and O[2] atom sites.

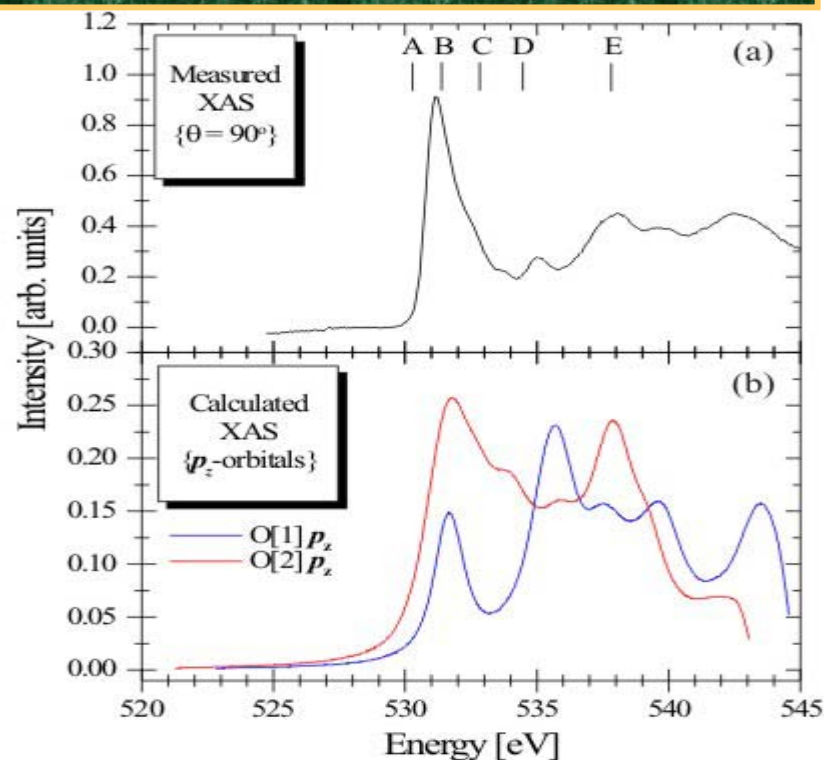


Figure 5.11. Comparison of (a) the experimental absorption spectra targeting the p_z orbitals ($\theta = 90$ degrees) with (b) the calculated absorption spectra of the p_z orbitals of the O[1] and O[2] atom sites.



XES of Sr_2RuO_4 : Theory and Experiment

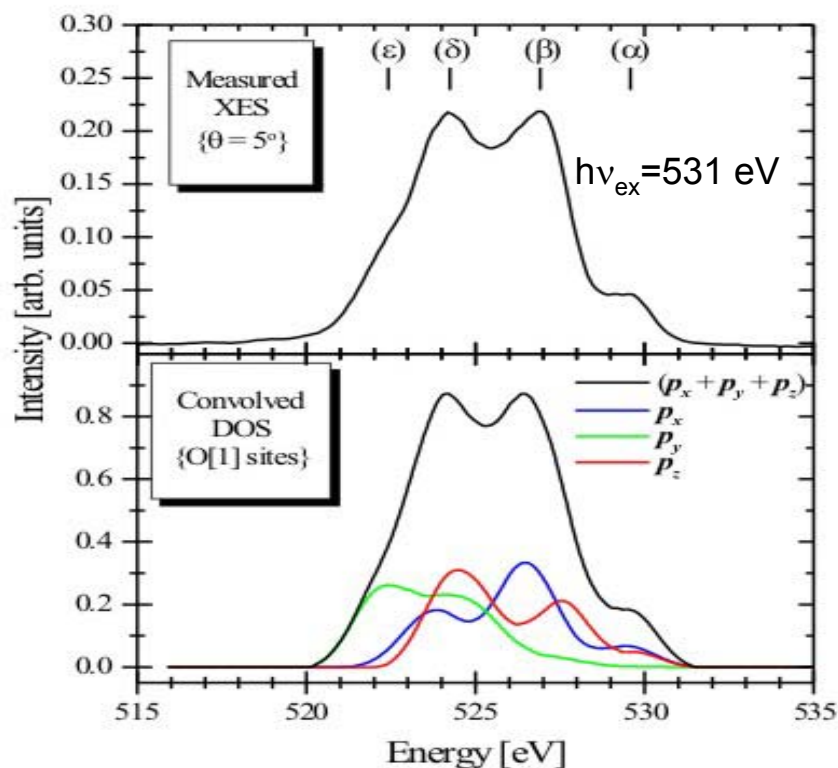


Figure 5.13. Comparison of (a) the experimental emission spectrum targeting the O[1] sites ($\theta = 5$ degrees) with (b) the convolved DOS of the p_x , p_y , and p_z orbitals of the O[1] atom site.

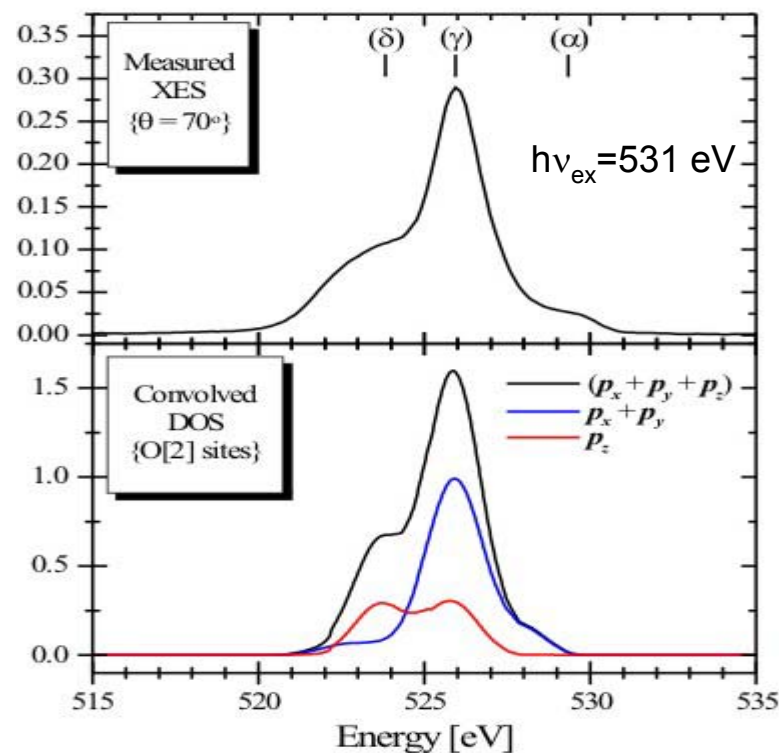
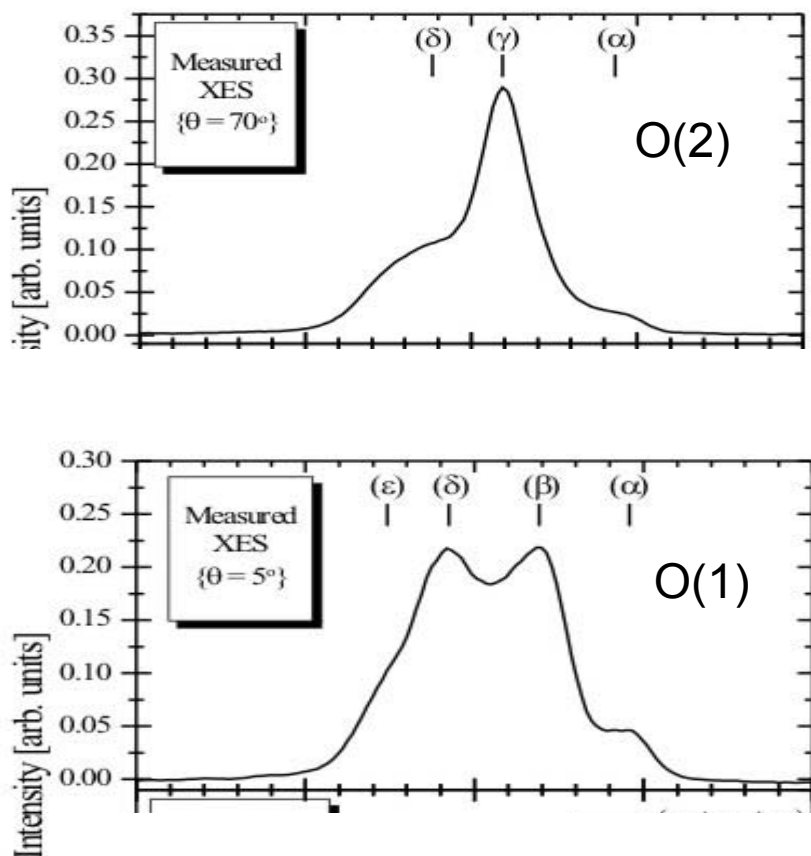


Figure 5.14. Comparison of (a) the experimental emission spectrum targeting O[2] sites ($\theta = 70$ degrees) with (b) the convolved DOS of the p_x , p_y , and p_z orbitals of the O[2] atom site.



XES Comparison: Angle vs. Energy



Kurmaev et al, PRB 57, 1558 (1998)

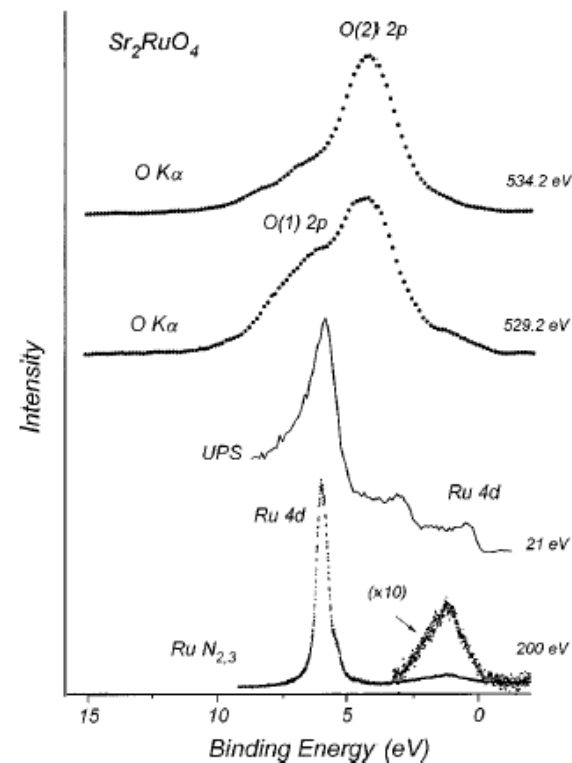


FIG. 4. The comparison of the experimental Ru $N_{2,3}$ XES (measured at $E=200$ eV), O $K\alpha$ XES (measured at $E=529.2$ and 534.2 eV) with the UPS of Sr_2RuO_4 excited at $E=21$ eV.



Observations

- ❑ Site determined by angle and/or by energy
- ❑ DFT gives a reasonable approximation to conduction band
- ❑ O(1) p_y PDOS small at E_F
- ❑ Hybridization between p_x and p_z orbitals at O(1)
- ❑ Hybridization between Ru and p_z at the O(2) site
- ❑ Theory is an essential tool



Layout of the New Tennessee- APS-Tulane Endstation (TAT) at Sector 4 of the APS



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Photon-in and Photon-out X-ray Spectroscopy in Material Sciences, Environmental Energy and Chemical Analysis
(October 19-20, 2004)

Experimental Parameters Controlled

Experimental Parameters	Implementation	Values
Polarization	CPU	↔ ↕ ↻ ↺
Magnetic Field	SC Octopole	4T, Any Direction
Scattering Angle	Chamber Rotation	25° – 170° (25-45, 56-77-107, 118-138, 149-169)
Inc. Angle-beam/sample	XYZ/Rot Manipulator	Any in optical plane
Temperature	Cryotip	4 – 400 K
Spot size	K/B pair	Emission 40 μm (H) x 20 μm (V) Absorption 10 μm (H) x 10 μm (V)
Detector	SX Emission Spectrometer	<i>or any other</i>



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Other Features of Endstation

- Sample load lock
- In-situ storage for 7 samples
- Video Assisted alignment of beam/sample/spectrometer
- Quick change of scattering Range
- Labview operating system for experimental control and data acquisition including:
 - Angular positioning of sample and scattering angle
 - Monochromator settings for input beam
 - Emission spectrometer settings
 - Magnetic field settings
 - Data Acquisition of emission spectra, sample current for TEY and integrated emission

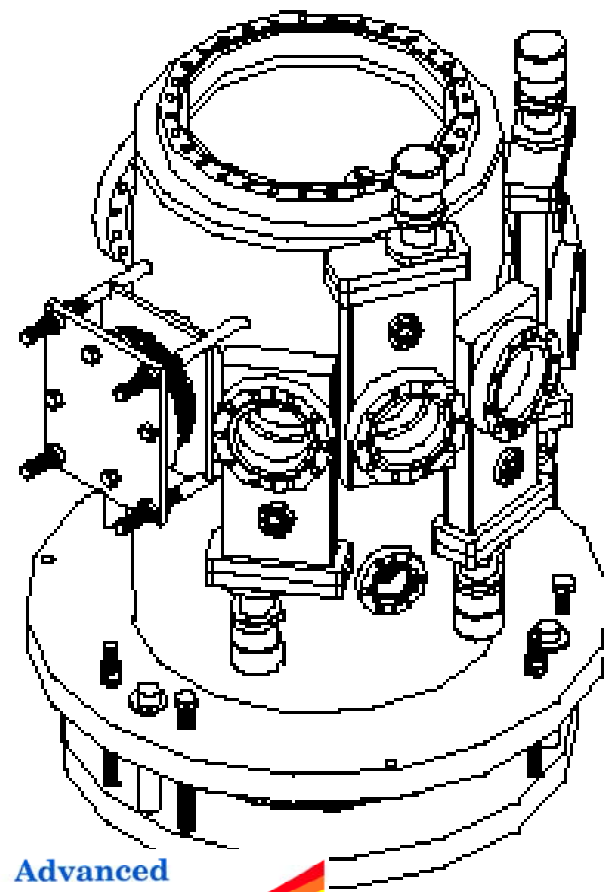
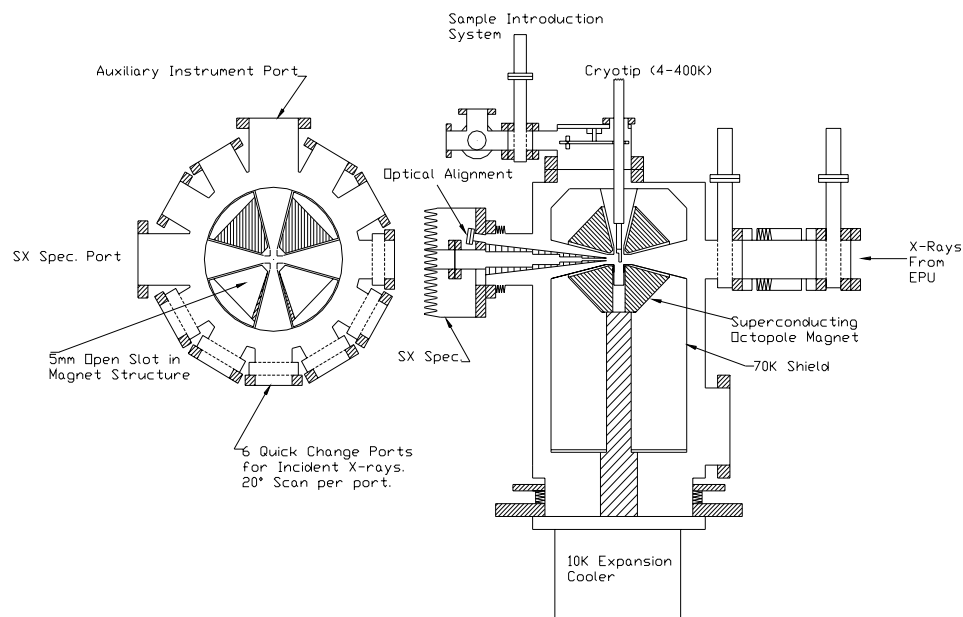


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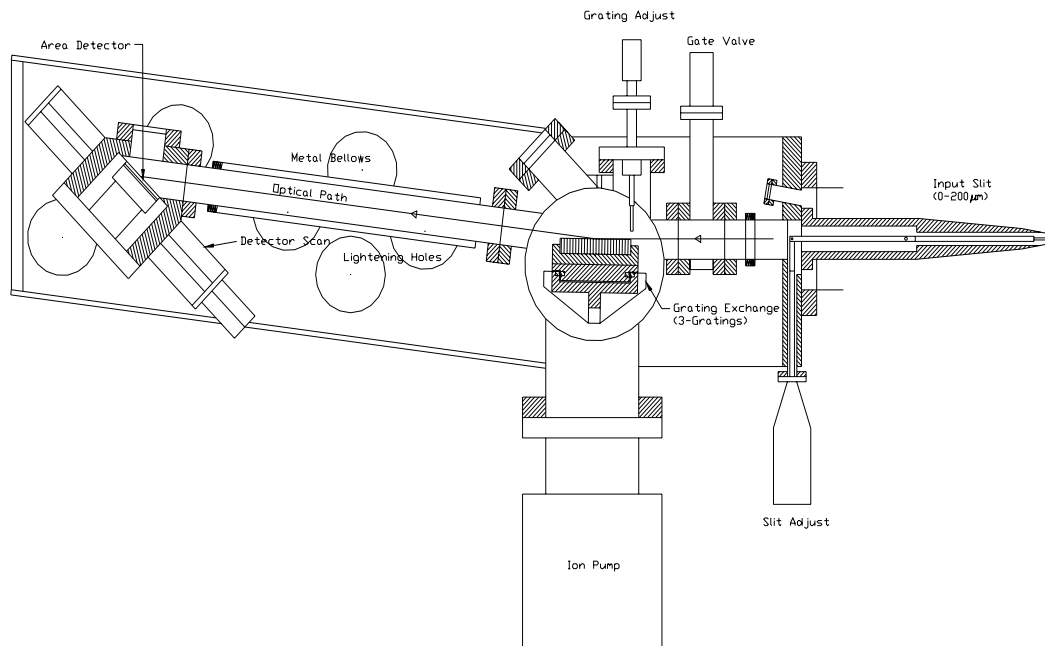
Endstation Schematics



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Spectrometer Schematic



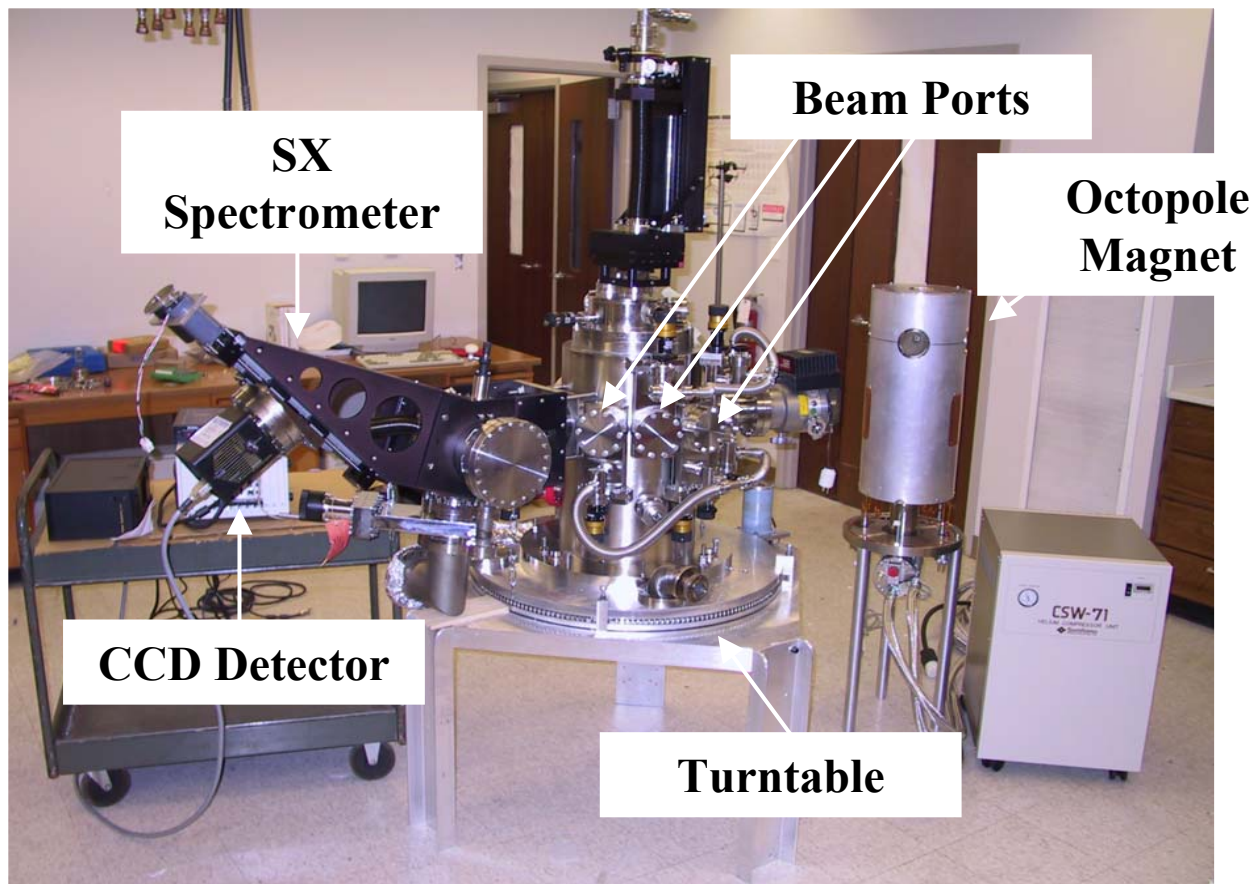
Schematic diagram of varied-line-space (VLS) grating spectrometer. It is compact, uses three gratings to cover an energy range from 50 to 1200 eV with a resolving power of 2000, uses a photon counting area detector for efficient detection of spectra, and can be used with either a variable input slit or in slitless operation



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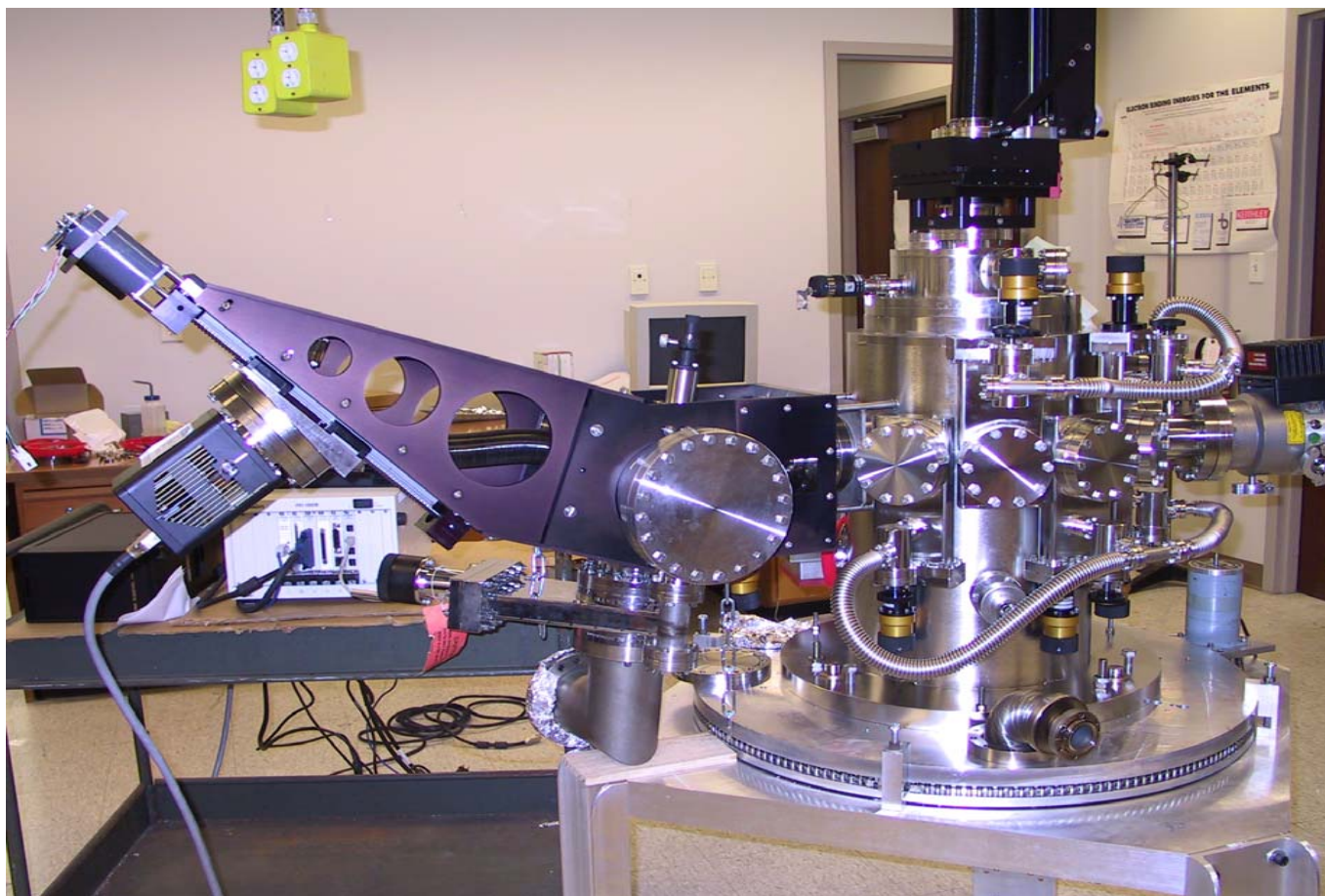
Angle Resolved Soft X-ray Spectroscopy Endstation



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Soft X-ray Spectrometer and Sample Chamber



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Photon-in and Photon-out X-ray Spectroscopy in Material Sciences, Environmental Energy and Chemical Analysis
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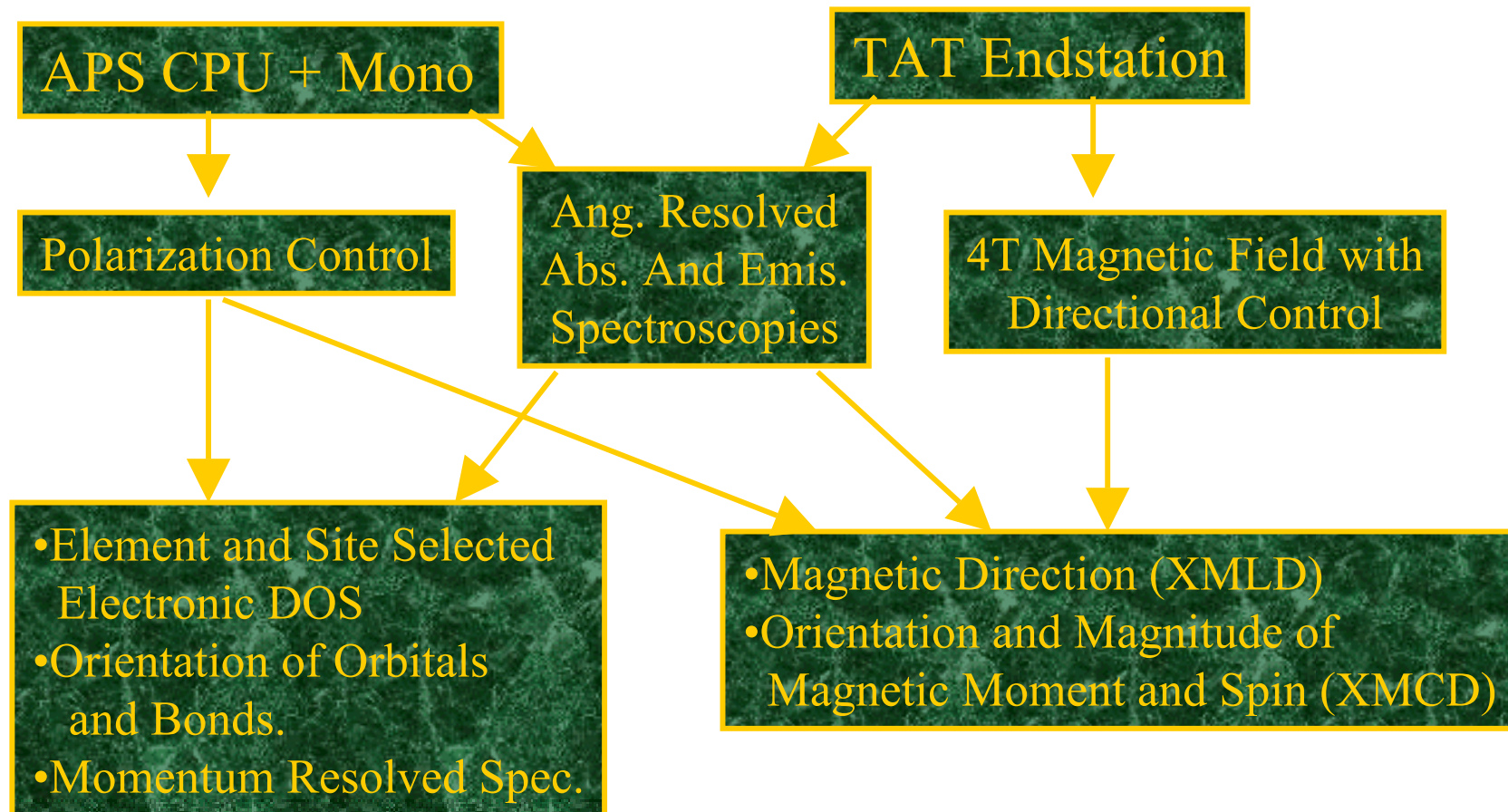
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Photon-in and Photon-out X-ray Spectroscopy in Material Sciences, Environmental Energy and Chemical Analysis
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The Future at TAT



Advanced
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